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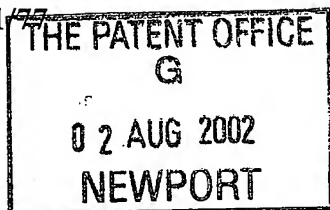
Signed

Andrew Giersey

Dated

11 February 2003





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1/77

Request for grant of a patent

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1. Your reference	84108/12380/04		
2. Patent application number (The Patent office will fill in this part)	02 AUG 2002		
3. Full name, address and postcode of the or of each applicant (underline all surnames)	EASTMAN KODAK COMPANY 343 STATE STREET ROCHESTER NEW YORK 14650-2201 UNITED STATES OF AMERICA		
Patents ADP number (if you know it) 00423020001			
If the applicant is a corporate body, give the country/state of its incorporation NEW JERSEY			
4. Title of the invention	METHOD FOR THE PREPARATION OF A PRINTING PLATE		
5. Name of your agent (if you have one)	H HAILE		
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	KODAK LIMITED PATENTS, W92-3A HEADSTONE DRIVE HARROW MIDDLESEX HA1 4TY		
Patents ADP number (if you know it) 08438236001			
6. If you are declaring priority from one or more earlier patent applications, give the country and date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of Filing (day / month / year)
7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application		Date of filing (day / month / year)
8. Is a statement of inventorship and of right to grant a patent required in support of this request? (Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))	YES		

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document.

Continuation sheets of this form

Description 19

Claim(s) 2

Abstract 1

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority Documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patent Form 9/77)

Request for substantive examination (Patent Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

H E Haile
Signature

01 Aug 2002
Date

12. Name and daytime telephone number of person to contact in the United Kingdom H HAILE 020 8424 4419

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METHOD FOR THE PREPARATION OF A PRINTING PLATE

FIELD OF THE INVENTION

This invention relates to a method for the preparation of a printing
5 plate and to a printing plate prepared by the method.

BACKGROUND OF THE INVENTION

Printing plates suitable for offset lithographic printing are known
which comprise a support having non-image areas which are hydrophilic and
10 image areas which are hydrophobic and ink-receptive.

The art of lithographic printing is based upon the immiscibility of
oil and water, wherein the oily material or ink is preferentially retained by the
image area and water or fountain solution is preferentially retained by the non-
image area. When a suitably prepared surface is moistened with water and an ink
15 is then applied the background or non-image area retains the water and repels the
ink while the image area accepts the ink and repels the water. The ink on the
image area is then transferred to the surface of a material upon which the image is
to be reproduced, such as paper, cloth and the like.

Commonly the ink is transferred to an intermediate material called
20 the blanket which in turn transfers the ink to the surface of the material upon
which the image is to be reproduced.

Inkjetting is the non-impact method for producing images by the
deposition of ink droplets on a substrate in response to digital signals.

JP-A-53015905 describes the preparation of a printing plate by
25 inkjetting an alcohol-soluble resin in an organic solvent onto an aluminum
printing plate.

JP-A-56105960 describes the formation of a printing plate by
inkjetting onto a support e.g. an anodised aluminum plate an ink capable of
forming an oleophilic image and containing a hardening substance such as epoxy-
30 soybean oil together with benzoyl peroxide or a photo-hardening substance such
as an unsaturated polyester.

EP-A-0 882 584 describes a method of preparing a printing plate comprising producing an oleophilic image on the surface of a support by inkjet printing the image on the surface using an aqueous solution or of a salt of a hydrophobic organic acid e.g. oleic acid.

U.S. Patent No. 6131514 describes a method of preparing a printing plate comprising producing an oleophilic image on the surface of a support by inkjet printing the image on the surface using an aqueous solution or aqueous colloidal dispersion of a polymer bearing water-solubilising groups wherein the water solubilising groups interact with the surface of the support thereby binding the polymer to the support and rendering the polymer insoluble.

PROBLEM TO BE SOLVED

Inkjet printing provides a rapid and simple way of preparing a printing plate directly from digital information on a computer which uses simpler and much less expensive equipment than commonly used computer-to-plate systems, which use high power lasers in the case of thermal effect platesetters, or lower power lasers together with a wet processing step in the case of visible light platesetters. However, it is desired to prepare plates with a long run life and with a greater tolerance to the fountain solutions used on lithographic presses than those prepared using salts of mono-basic organic acids as described in EP-A-0 882 584. It is also desired to reduce the risk of the inkjet jets becoming clogged which can happen when writing fluids containing polymeric substances dry out at the writing head.

It is preferred that the inkjet writing fluids are water-based for environmental and health reasons, and also to avoid the excessive evaporation and drying out at the jets which can occur with moderately volatile organic solvents.

SUMMARY OF THE INVENTION

The invention provides a method for the preparation of a printing plate comprising inkjet printing an oleophilic image on a surface of a support by applying to the support an aqueous solution or aqueous colloidal dispersion of an

oleophilising compound on the surface of the support and drying the applied solution or dispersion, such that on drying the area of the surface to which the solution or dispersion was applied becomes lithographic ink-accepting, characterised in that the oleophilising compound has the chemical structure ..

5



or



10 wherein

M is H or a cation;

each of l, m and n independently is 0 or 1,

provided that $l+m+n =$ at least 1;

each of R, R' and R'' independently is -H, -B or -L-B;

15

L is a linking group selected from alkylene, alkyleneoxy, thio, sulfonyl, sulfinyl, sulfoxyl, amido, oxyamido, carbamoyl, sulfonylamido, aminosulfonyl, aminosulfonylamido, hydrazinylsulfonyl, carboxyl, oxycarbonyl, carbonyl, carboxyhydrazinyl, amino, thiocarbonyl, sulfamoylamino, sulfamoyl, thiocarbamoyl, any one of said linking groups being substituted or unsubstituted;

20

and,

B is a hydrophobic group comprising 8 or more carbon atoms,

provided that at least one of R, R' and R'' is present and has the structure -B or -L-B.

25

DETAILED DESCRIPTION OF THE INVENTION

The carboxylic acid and sulfonic acid groups of the oleophilising compound may be wholly or partially ionised as carboxylate ions and sulfonate ions, respectively. When the acid groups are ionised, examples of M include a cation selected from substituted or unsubstituted ammonium ions, and metal ions e.g. alkali metal ions such as sodium or potassium.

30

In a preferred embodiment, the linking group -L is selected from alkylene, amino, amido or carbamoyl, any one of said linking groups being substituted or unsubstituted. Examples of such groups include methylene (-CH₂-), >CHCOOH, -NHCOCH₂-, and -NR'''COCH₂- wherein R''' is

5 -CH(CO₂Na)CH₂(CO₂Na) and >NCOCH₂CH(CO₂Na)(SO₃Na) .

The term hydrophobic group is widely understood in the science of surface chemistry. The hydrophobic group may be an aliphatic and/or aromatic hydrocarbon group that may be saturated or unsaturated. Preferred groups include alkyl groups having from 8 to 40 carbon atoms. The hydrophobic group may be

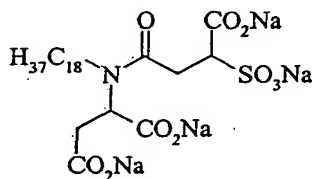
10 substituted. Suitable substituents include ester, ether and substituted amide and carbamoyl groups provided the substituents do not destroy the hydrophobic nature of the hydrophobic group. An example of a preferred substituent is -CONHCH(COOM)₂ wherein M is as defined above.

The oleophilising compound may have further carboxylic,

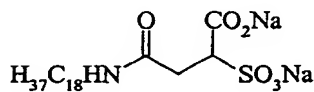
15 sulphuric or sulphonic acid groups or salts thereof. It is necessary to retain a suitable hydrophilic-lipophilic balance in the oleophilising compound, so additional acid or acid salt groups may require larger or additional hydrophobic groups in the molecule. The further acid groups may be wholly or partially esterified. When the acid groups are esterified, examples of M include substituted

20 or unsubstituted alkyl groups such as methyl, ethyl, propyl and butyl.

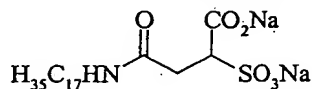
Suitable oleophilising compounds include the surfactant AEROSOLTM 22, which has the structure



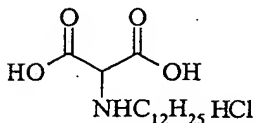
25 the surfactant AEROSOLTM 18, which has the structure



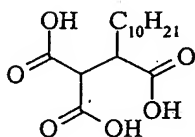
the surfactant EMCOL™ K8300, which has the structure



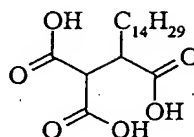
the compounds 2 to 4:



Compound 2



Compound 3



Compound 4

and the Compounds 5, 7, 9, 11, 12, 14, 16 and 18 whose preparation is described in Preparative Example 1, below.

It is necessary that the salt of the hydrophobic organic acid is in the form of an aqueous solution or a stable colloidal dispersion, so that it can pass through the jets of the printer head.

The oleophilising compounds may be present in the aqueous composition in an amount from 0.005 to 5, preferably from 0.02 to 1 % by weight.

While water is the preferred aqueous carrier medium, the aqueous composition may comprise one or more water miscible solvents e.g. a polyhydric alcohol such as ethylene glycol, diethylene glycol, triethylene glycol or

trimethylol propane. The amount of aqueous carrier medium in the aqueous composition may be in the range from 30 to 99.995, preferably from 50 to 95 % by weight.

Jet velocity, separation length of the droplets, drop size and stream stability are greatly affected by the surface tension and the viscosity of the aqueous composition. Inkjet inks suitable for use with inkjet printing systems may have a surface tension in the range from 20 to 60, preferably from 30 to 50 dynes/cm. Control of surface tensions in aqueous inks may be accomplished by additions of small amounts of surfactants. The level of surfactants to be used can be determined through simple trial and error experiments. Anionic and nonionic

surfactants may be selected from those disclosed in US Patent Nos. 5324349, 4156616 and 5279654 as well as many other surfactants known in the inkjet art. Commercial surfactants include the SURFYNOL™ range from Air Products; the ZONYL™ range from DuPont; the FLUORAD™ range from 3M and the
5 AEROSOL™ range from Cyanamid.

The viscosity of the ink is preferably no greater than 20 centipoise e.g. from 1 to 10, preferably from 1 to 5 centipoise at room temperature.

The ink may comprise other ingredients. A humectant or co-solvent may be included to help prevent the ink from drying out or crusting in the orifices
10 of the print head. A biocide, such as PROXEL™ GXL from Zeneca Colours may be added to prevent unwanted microbial growth which may occur in the ink over time. Additional additives which may be optionally present in the ink include thickeners, pH adjusters, buffers, conductivity enhancing agents, anti-kogation agents, drying agents and defoamers.

15 The aqueous composition is employed in inkjet printing wherein drops of the composition are applied in a controlled fashion to the surface of the support by ejecting droplets from a plurality of nozzles or orifices in a print head of an inkjet printer.

Commercially available inkjet printers use several different
20 schemes to control the deposition of the ink droplets. Such schemes are generally of two types: continuous stream and drop-on-demand.

In drop-on-demand systems, a droplet of ink is ejected from an orifice directly to a position on the ink receptive layer by pressure created by, for example, a piezoelectric device, an acoustic device, or a thermal process
25 controlled in accordance with digital signals. An ink droplet is not generated and ejected through the orifices of the print head unless it is needed. Ink-jet printing methods and related printers are commercially available and need not be described in detail.

The aqueous composition may have properties compatible with a
30 wide range of ejecting conditions, e.g. driving voltages and pulse widths for thermal inkjet printers, driving frequencies of the piezoelectric element for either a

drop- on-demand device or a continuous device, and the shape and size of the nozzle.

The support may be any support suitable for printing plates. Typical supports include metallic and polymeric sheets or foils, polyester films, and paper-based supports.

A support having a metallic surface may be used. Preferably, the metallic surface is oxidised.

In a preferred embodiment of the invention, a support having an anodized aluminum surface is employed.

A lithographic printing plate having an anodized aluminum surface is typically formed of aluminum which has been grained, for example by electrochemical graining, and then anodized, for example, by means of anodizing techniques employing sulfuric acid and/or phosphoric acid. Methods of both graining and anodizing are very well known in the art and need not be further described herein.

In another preferred embodiment of the invention, the support bears a hydrophilic coating on its surface and the inkjet writing fluid is jetted onto the hydrophilic layer, which is rendered oleophilic where the fluid is applied. The hydrophilic layer may comprise water-soluble polymers such as gelatin or polyvinyl alcohol, and the polymers may be crosslinked to render them insoluble once dried. The layer may contain inorganic particles such as silica, alumina, titanium dioxide or kaolin. Hardened hydrophilic layers containing inorganic particles are disclosed by Staehle in US Patent 3971660.

A coated hydrophilic layer suitable for the invention may or may not comprise a crosslinked cationic polymer, in particular polyethyleneimine, as described in our copending simultaneously filed GB patent application entitled "Method and Substrate for the Preparation of a Printing Plate"(Docket 84218).

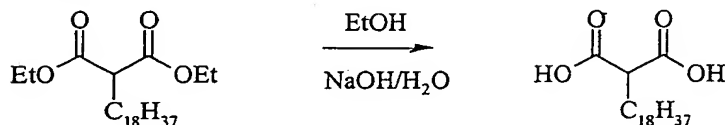
After writing the image to the printing plate, the printing plate may be inked with printing ink in the normal way, and the plate used on a printing press. Before inking, the plate may be treated with an aqueous solution of natural gum, such as gum acacia, or of a synthetic gum such as carboxymethyl cellulose, as is well known in the art of printing - see for example Chapter 10 of "The

Lithographer's Manual", edited by Charles Shapiro and published by The Graphic Arts Technical Foundation, Inc., Pittsburgh, Pennsylvania (1966).

The invention is further illustrated by way of example as follows.

5 Preparative Example 1

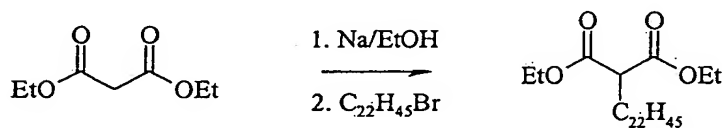
Compound 5



Compound 5

A solution of 2-octadecylpropanedioic acid diethyl ester (1.5g, 3.64mmol) in EtOH (ethyl alcohol) (8ml) was added dropwise to a solution of NaOH (291mg, 7.27mmol) in a mixture of EtOH and H₂O (13:1.7ml) and the solution stirred for 18hrs. The solvent was removed under reduced pressure, the residue diluted with H₂O and extracted with DCM (dichloromethane). The aqueous phase was acidified with dilute HCl, extracted with EtOAc (ethyl acetate), dried (MgSO₄) and removal of the solvent under reduced pressure yielded the desired product as a white solid (1.20g, 93%).

Compound 6

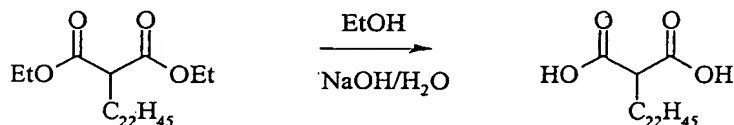


Compound 6

A solution of diethylmalonate (10g, 62mmol) in EtOH (10ml) was added dropwise to a solution of NaOEt (3.83g, 71mmol) in EtOH (50ml) and stirring continued at reflux for 1hr. The solution was cooled and 1-bromodocosane (26.8g, 69mmol) in EtOH (10ml) was added dropwise and the solution heated at reflux for a further 18hrs. The solution was filtered, the solvent removed under

reduced pressure, the residue diluted with DCM, washed with water, 2M NaOH solution, dried (MgSO₄) and concentrated under reduced pressure to give the product as a clear oil which was used without further purification.

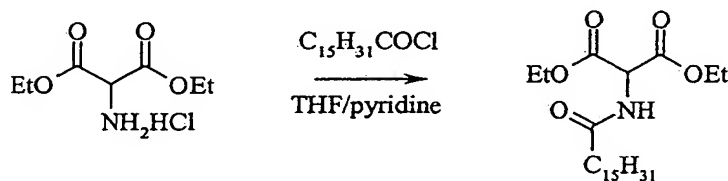
5 Compound 7



Compound 7

10 A solution of compound 6 (1.60g, 3.41mmol) in EtOH (7.5ml) was added dropwise to a solution of NaOH (341mg, 8.53mmol) in a mixture of EtOH and H₂O (15:2ml) and the solution stirred for 18hrs. The solvent was removed under reduced pressure and the residue diluted with H₂O and extracted with DCM. The aqueous phase was acidified with dilute HCl, extracted with EtOAc, dried (MgSO₄) and concentrated under reduced pressure to yield the desired product as
15 a white solid (1.35g, 96 %).

Compound 8



Compound 8

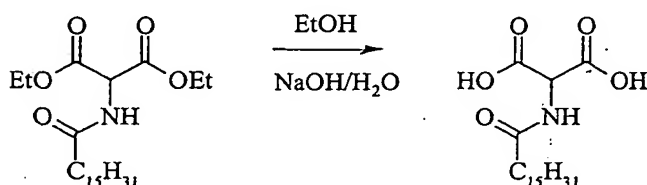
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A solution of the palmitoyl chloride (2.58g, 9.48mmol) in THF (tetrahydrofuran) (43ml) was added dropwise to a solution of diethylaminomalonate hydrochloride (2g, 9.48mmol) in pyridine (43ml) at room temperature and stirring continued for 18hrs. The reaction mixture was poured

into H₂O:HCl (1000:100ml), stirred for 3hrs, and the solid collected by filtration to give the desired product as a white solid (3.81g, 97%).

Compound 9

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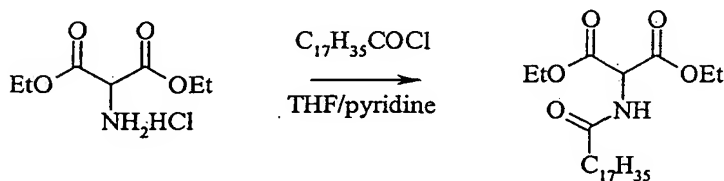


Compound 9

A solution of Compound 9 (1.5g, 3.65mmol) in EtOH (8ml) was added dropwise to a solution of NaOH (320mg, 7.99mmol) in a mixture of EtOH and H₂O (18:2ml) and the solution stirred for 18hrs. The solvent was removed under reduced pressure and the residue diluted with H₂O and extracted with DCM. The aqueous phase was acidified with dilute HCl, extracted with EtOAc, dried (MgSO₄) and concentrated under reduced pressure to yield the desired product as a white solid (1.25g, 100%).

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Compound 10



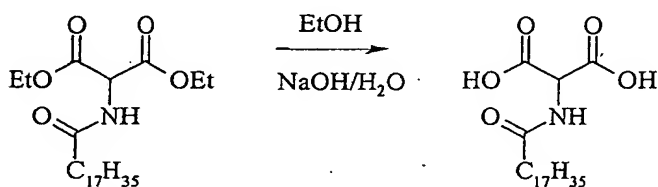
Compound 10

A solution of stearic acid (5g, 17.61mmol) in thionyl chloride (35ml) was stirred at reflux for 1hr, the solvent removed under reduced pressure and the residue stripped with petrol to give the acid chloride. A solution of the acid chloride in THF (35ml) was added dropwise to a solution of diethylaminomalonate hydrochloride (3.73g, 17.61mmol) in pyridine (35ml) at

room temperature and stirring continued for 18hrs. The reaction mixture was poured into H₂O:HCl (1000:100ml), stirred for 3hrs, and the solid collected by filtration. Recrystallisation (MeOH) gave the desired product as a white solid (3.47g, 45%).

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Compound 11



Compound 11

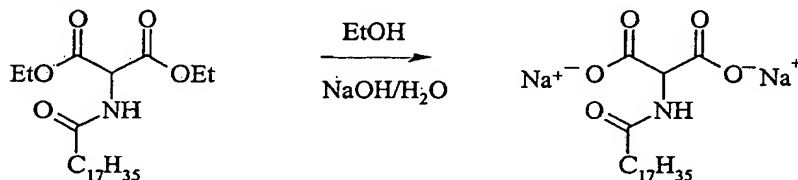
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A solution of Compound 11 (3g, 6.8mmol) in EtOH (14ml) was added dropwise to a solution of NaOH (600mg, 14.97mmol) in a mixture of EtOH and H₂O (20:4ml) and the solution stirred at 60 degrees for 18hrs. The solvent was removed under reduced pressure and the residue diluted with H₂O and extracted with DCM. The aqueous phase was acidified with 2M HCl, extracted with

15

EtOAc, dried (MgSO₄) and removal of the solvent under reduced pressure yielded the desired product as a white solid (2.3g, 88%).

Compound 12



Compound 12

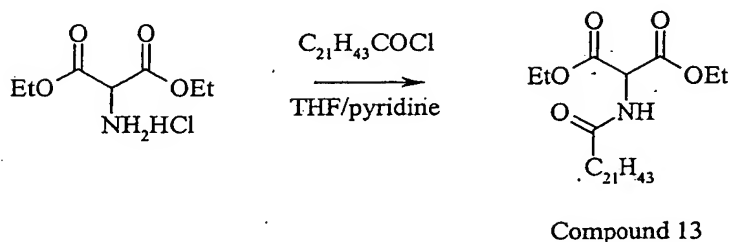
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A solution of Compound 11 (1.5g, 3.90mmol) in EtOH (7.0ml) was added dropwise to a solution of NaOH (300mg, 7.49mmol) in a mixture of EtOH and H₂O (10:2ml) and the solution stirred at 60 degrees for 18hrs. The solvent was

removed under reduced pressure to the yield the product as a white solid (1.23, 97 %).

Compound 13

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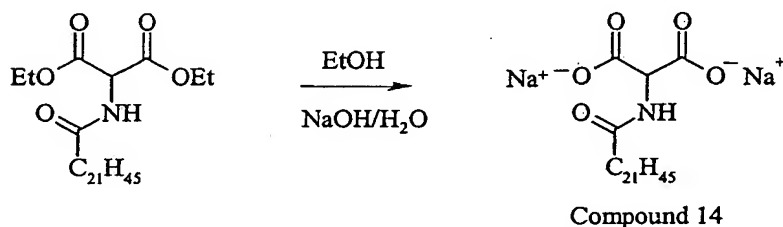
10 A solution of behemic acid (5g, 14.68mmol) in thionyl chloride (30ml) was stirred at reflux for 1hr, the solvent removed under reduced pressure and the residue stripped with petrol to give the acid chloride.

15 A solution of the acid chloride in THF (35ml) was added dropwise to a solution of diethylamino malonate hydrochloride (3.11g, 14.68mmol) in pyridine (35ml) at room temperature and stirring continued for 18hrs. The reaction mixture was poured into H₂O:HCl (1000:100ml), stirred for 3hrs, and the solid collected by filtration.

- Recrystallisation (methyl alcohol) gave the desired product as a white solid (8g, 100%).

Compound 14

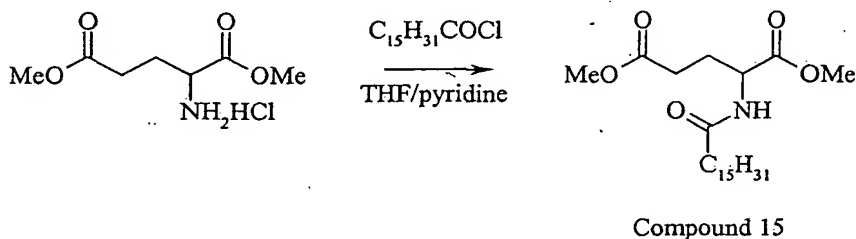
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A solution of Compound 13 (2.0g, 4.02mmol) in EtOH (8ml) was

added dropwise to a solution of NaOH (354mg, 8.85mmol) in EtOH and H₂O (15:2ml) and the solution stirred at 35 degrees for 18hrs. The solvent was removed under reduced pressure to yield the product as a white solid (1.65g, 93 %).

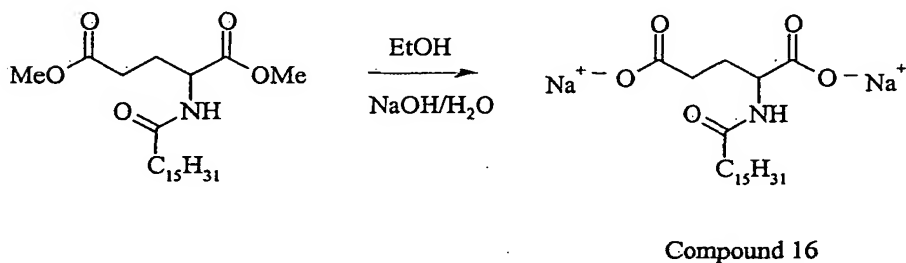
5 Compound 15



10 A solution of palmitoyl chloride (6.47g, 23.62mmol) in THF (60ml) was added dropwise to a solution of L-glutamic acid dimethyl ester (5.0g, 23.62mmol) in pyridine (60ml) at room temperature and stirring continued for 18hrs. The reaction mixture was poured into H₂O:HCl (1000:100ml), stirred for 3hrs, and the solid collected by filtration to give the desired product as a white solid (11.64g, 100%).

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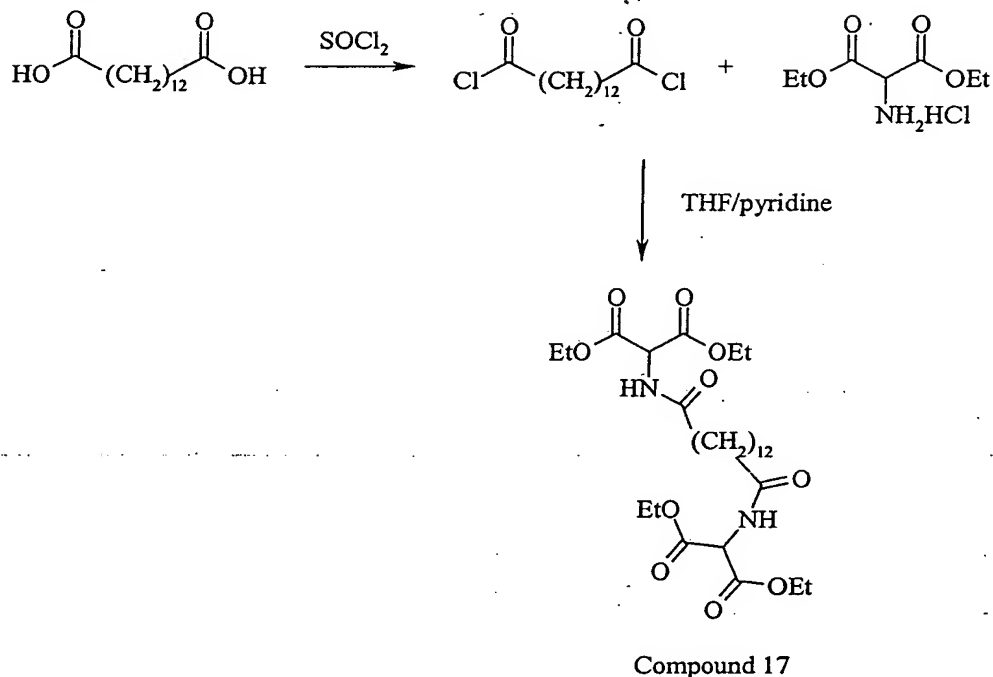
Compound 16



20 A solution of Compound 15 (3.0g, 7.26mmol) in EtOH (10ml) was added dropwise to a solution of NaOH (640mg, 15.98mmol) in a mixture of EtOH and H₂O (20:4ml) and the solution stirred at 35 degrees for 18hrs. The solvent was

removed under reduced pressure to yield the product as a white solid (2.67g 96%).

Compound 17



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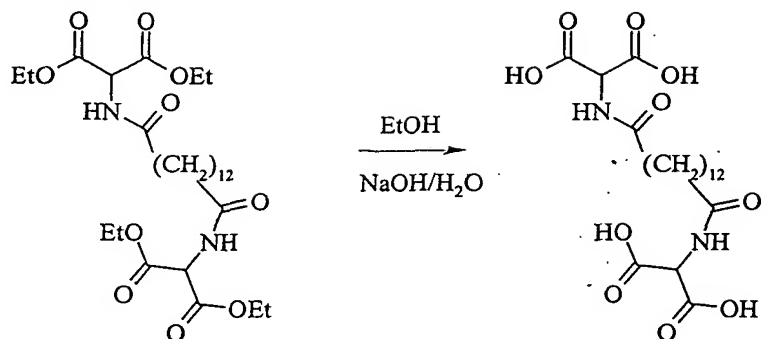
A solution of 1,12-dodecanoic dicarboxylic acid (2g, 7.74mmol) in thionyl chloride (15ml) was stirred at reflux for 1hr, the solvent was removed under reduced pressure and the residue stripped with petrol to give the acid chloride.

10

A solution of the acid chloride in THF (12ml) was added dropwise to a solution of diethylaminomalonate hydrochloride (3.28g, 15.48mmol) in pyridine (30ml) at room temperature and stirring continued for 18hrs. The reaction mixture was poured into $\text{H}_2\text{O:HCl}$ (1000:100ml), stirred for 3hrs, and the solid collected by filtration to yield the required product as a white solid (4.15g, 100%)

15

Compound 18



Compound 18

5 A solution of Compound 17 (3g, 3.49mmol) in EtOH (8.0ml) was added dropwise to a solution of NaOH (840mg, 20.97mmol) in a mixture of EtOH and H₂O (20:6ml) and the solution stirred for 18hrs. The solvent was removed under reduced pressure and the residue diluted with H₂O and extracted with DCM. The aqueous phase was acidified with dilute HCl, extracted with EtOAc, dried (MgSO₄) and concentrated under reduced pressure to yield the desired product as
10 a white solid.

Example 1

Solutions of the test compounds were prepared by dissolving them in water at a concentration of 0.5% w/w. If the test compound was in the form of
15 a free acid, sufficient sodium hydroxide solution was added to convert all the acid to the sodium salt. Each solution was applied to a portion of a hydrophilic substrate with a small squirrel-hair paintbrush, and allowed to dry. Two hydrophilic substrates were used, they were
(A) grained, anodised aluminum, as commonly used for making printing plates,
20 and
(B) polyethylene terephthalate photographic film base coated from aqueous solution with the following coverages of the stated substances:

Cationic colloidal silica Ludox CL™	3.0 g/m ²
Polyethyleneimine (used as a 5% w/w solution and adjusted to pH 6.5 with sulphuric acid)	0.6 g/m ²
bis(vinylsulphonyl)methane (hardener)	0.05 g/m ²

5

hereinafter referred to as Film B.

The portions of hydrophilic substrate were gently wiped with a piece of cotton wool which was wetted with water. A little black lithographic
10 printing ink was then applied to the cotton wool, and the inked cotton wool pad rubbed gently over the substrate. The test was then repeated except the cotton wool was wetted with lithographic press fount solution (Varn International™ Universal Pink Fount Solution, diluted 1 + 15 with water).

This test was carried out with the following compounds according
15 to the invention: AEROSOL™ 22, AEROSOL 18, EMCOL™ K8300, and compounds 2, 3, 4, 5, 7, 14, 16, and 18.

In the case that the cotton wool was wetted with water and also in the case that the cotton wool was wetted with fount solution, in the area of the substrate to which the solution of each oleophilising compound had been applied,
20 a clear black mark of adhering lithographic ink was observed, while the background areas of the substrate remained unmarked and wetted with water-or fount solution. This demonstrated that the compounds showed an oleophilising effect on the substrates used, and so were potentially useful for making lithographic printing plates by inkjet application.

25 The test was also carried out with the following comparative compounds:

Sodium dodecyl sulphate

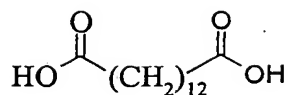
Sodium benzene dodecyl sulphate

Tri-isopropyl naphthalene sulphonate

30 Dioctyl sulphosuccinate, sodium salt

Sodium stearate

Comparative compound 1



For all the comparative compounds, when the test was done using the film substrate, and water as the wetting liquid, in the area of the substrate to which the solution of the test compound had been applied, a clear black mark of adhering lithographic ink was observed, while the background areas of the substrate remained unmarked and wetted with water.

However for all the comparative compounds, on both film and aluminum substrates, when fount solution was used as the wetting liquid, the area where the solution of compound had been applied remained clear of lithographic printing ink, no ink adhered to either substrate, demonstrating a complete absence of lithographic effect in the presence of the fount solution.

The results show how compounds for use in the invention show a much superior lithographic effect to similar compounds having only one acid group, or two carboxylic acid groups spaced widely apart.

Example 2

The test described in Example 1 was carried out using a number of compounds according to the invention using hydrophilic substrate C, similar to hydrophilic substrate B, and which consisted of polyethylene terephthalate photographic film base coated from aqueous solution with the following coverages of the stated substances:

Cationic colloidal silica Ludox CL™	4.0 g/m ²
Polyethyleneimine (used as a 5% w/w solution and adjusted to pH 6.5 with sulphuric acid)	0.4 g/m ²
bis(vinylsulphonyl)methane (hardener)	0.033 g/m ²

hereinafter referred to as Film C.

The resulting mark of adsorbed lithographic printing ink was then subjected to a wet abrasion test to estimate its robustness. A swab of soft cotton

fabric was attached to a weight and moved to and fro over the surface, and the number of abrasion strokes required to remove the centre of the mark of adsorbed lithographic printing ink was recorded. The results were as follows:

Compound	Number of strokes
2	10
3	2
4	2
5	2
7	2
9	28
11	42
12	37
14	50
16	59
18	84

5

Compounds 2, 9, 11, 12, 14, 16, and 18 were examples of preferred compounds in which the linking group bound to the hydrophobic group is bonded to the carbon atoms between the acid groups via a nitrogen atom, and all showed better abrasion resistance than the substances which did not have that structure.

10 Example 3:

An inkjet writing fluid was prepared as follows:

To 11.5 ml of water was added 2.5 ml of a 4% w/w aqueous solution of AEROSOL™ 22, 2 ml of ethanediol, and 4 ml of 2% w/w aqueous solution of the dye PHLOXINE™ B. (The AEROSOL™ 22 was the
15 oleophilising compound, ethanediol a humectant, and the dye was present to make the fluid visible on the plate).

The black cartridge of a Lexmark Z43 inkjet printer was emptied, the plastic foam removed, and residual ink washed out. It was refilled with the above writing fluid and a wad of cotton wool in place of the foam. The cartridge
20 was replaced in the printer, and a test pattern was printed onto a sheet of Film B as described in Example 1.

When the test pattern had dried, the resulting polyester film printing plate was mounted on the plate cylinder of a Heidelberg T-Offset printing

press, the press rollers were inked up using fountain solution as described in Example 1 and K&ETM Novaquick 123W oil-based black ink, and printing started. Clean prints were obtained from the first impression, and 2000 copies of the test pattern were printed without noticeable deterioration.

5 Example 4

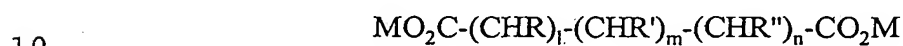
 Solutions of the test compounds were prepared by dissolving them in water at a concentration of 0.5% w/w. If the test compound was in the form of a free acid, sufficient sodium hydroxide solution was added to convert all the acid to the sodium salt. Each solution was applied using a small squirrel-hair
10 paintbrush to a separate part of a grained, anodized aluminum plate, so as to form a mark or pattern, and allowed to dry.

 The plate was mounted on the printing press as described in Example 3, and the press run as described in Example 3. Clean prints of the applied marks were obtained. The press was run for 8000 impressions, and the
15 approximate number of impressions noted when each mark showed some sign of wear. The results are shown in the Table:

Compound	Number of impressions
EMCOL K8300	400
2	>8000
9	4000
12	7000
18	400

CLAIMS

1. A method for the preparation of a printing plate comprising inkjet printing an oleophilic image on a surface of a support by applying to the support an aqueous solution or aqueous colloidal dispersion of an oleophilising compound on the surface of the support and drying the applied solution or dispersion, such that on drying the area of the surface to which the solution or dispersion was applied becomes lithographic-ink-accepting, characterised in that the oleophilising compound has the chemical structure



or



wherein

M is H or a cation;
 15 each of l, m and n independently is 0 or 1,
 provided that $l+m+n =$ at least 1;
 each of R, R' and R" independently is -H, -B or -L-B;
 L is a linking group selected from alkylene, alkyleneoxy, thio, sulfonyl, sulfinyl, sulfoxyl, amido, oxyamido, carbamoyl, sulfonylamido, aminosulfonyl, aminosulfonylamido, hydrazinylsulfonyl, carboxyl, oxycarbonyl, carbonyl, carboxyhydrazinyl, amino, thiocarbonyl, sulfamoylamino, sulfamoyl, thiocarbamoyl, any one of said linking groups being substituted or unsubstituted;
 20 and,

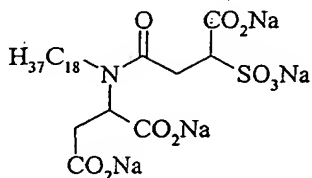
B is a hydrophobic group comprising 8 or more carbon atoms,
 25 provided that at least one of R, R' and R" is present and has the structure -B or -L-B.

2. A method according to claim 1 wherein the linking group L is selected from alkylene, amino, amido or carbamoyl, any one of said linking groups being substituted or unsubstituted.

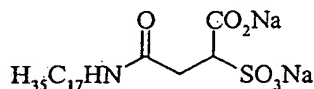
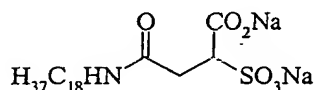
30 3. A method according to claim 1 wherein the linking group L is selected from $-\text{CH}_2-$, $>\text{CHCOOH}$, $-\text{NHCOCH}_2-$, $-\text{NR}'''\text{COCH}_2-$ wherein R''' is $-\text{CH}(\text{CO}_2\text{Na})\text{CH}_2(\text{CO}_2\text{Na})$, and $>\text{NCOCH}_2\text{CH}(\text{CO}_2\text{Na})(\text{SO}_3\text{Na})$.

4. A method according to any one of the preceding claims wherein the hydrophobic group is a substituted or unsubstituted alkyl group having from 8 to 40 carbon atoms.

5. A method according to claim 1 wherein the oleophilising compound is selected from



10



and compounds 2, 3, 4, 5, 7, 9, 11, 12, 14, 16 and 18 defined above.

15 6. A method according to any one of the preceding claims wherein the oleophilising compound is present in the aqueous solution or aqueous colloidal dispersion in an amount from 0.005 to 5 % by weight.

20 7. A method according to any one of the preceding claims wherein the aqueous solution or aqueous colloidal dispersion has a surface tension in the range from 20 to 60 dynes/cm.

8. A method according to any one of the preceding claims wherein the support is selected from metallic and polymeric sheets and foils, polyester films, and paper-based supports.

25 9. A printing plate obtainable by as method according to any one of the preceding claims.

METHOD FOR THE PREPARATION OF A PRINTING PLATE

ABSTRACT

A method for the preparation of a printing plate comprises inkjet
5 printing an oleophilic image on a surface of a support by applying to the support
an aqueous solution or aqueous colloidal dispersion of an oleophilising compound
on the surface of the support and drying the applied solution or dispersion, such
that on drying the area of the surface to which the solution or dispersion was
applied becomes lithographic ink-accepting, characterised in that the oleophilising
10 compound has the chemical structure



or



15

wherein

M is H or a cation;

each of l, m and n independently is 0 or 1,

provided that $l+m+n =$ at least 1;

20

each of R, R' and R" independently is -H, -B or -L-B;

L is a linking group selected from alkylene, alkyleneoxy, thio,
sulfonyl, sulfinyl, sulfoxyl, amido, oxyamido, carbamoyl, sulfonylamido,
aminosulfonyl, aminosulfonylamido, hydrazinylsulfonyl, carboxyl, oxycarbonyl,
carbonyl, carboxyhydrazinyl, amino, thiocarbonyl, sulfamoylamino, sulfamoyl,
25 thiocarbamoyl, any one of said linking groups being substituted or unsubstituted;
and,

B is a hydrophobic group comprising 8 or more carbon atoms,
provided that at least one of R, R' and R" is present and has the structure -B or
-L-B.